Communications in Inorganic Synthesis http://dx.doi.org/10.21060/cis.2016.431

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Self-assembly of two New Zinc coordination Polymers Based on N-[(3-Pyridine)-sulfonyl]amino Acid: Structure and Fluorescence

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Abstract: Two new zinc coordination polymers based on N-[(3-Pyridine)-sulfonyl]amino acid ligand have been synthesized and characterized by single-crystal X-ray diffraction and elemental analysis. The results show that the **1** is a two-dimensional structure coordination polymer and synthesized under room temperature condition; the **2** is a three-dimensional structure coordination polymer and synthesized under hydrothermal synthesis condition. These two structures are formed by 4,4'-dipyridy and 4,4'-azpy for **1** and **2**, respectively. A structural comparison of these two coordination polymers suggests that different reaction temperatures play important role in the construction of resulting architectures of **1** and **2**. Fluorescence measurements show that **1** has medium fluorescent emission at 374 nm and **2** has medium fluorescent emission at 438 nm.

Keywords: Synthesis, Crystal Structure, Fluorescence, Polymer

Supplementary material: X-Ray;XRD;IR

1. Introduction

Amino acids are the basic unit of building blocks of proteins, giving a specific protein molecular structure and morphology, so that its molecules with biological activity.[1] Further, amino acid and its derivatives can treat cancer.[2-4] Fluorescent probes are widely used to study protein changes and identification information N-terminal peptide residues.[5-7] From the 1970s to the present, the sulfonation of N-substituted amino acid complexes became an important subject to study in the world.[8] N-sulfonylated amino acid refers to the introduction of sulfonyl in the nitrogen-containing carboxylic acid ligands. From the viewpoint of biological effects, the N-sulfonylated amino acid not only contains the peptide bond, but also the carboxyl-terminal is very similar to peptide chain. So, N-sulfonylated amino acid and its derivatives are a very promising ligand.[9-11] Studies have shown that when the amino acid changes, the protein molecules will lose the biological activity. At the same time, the fluorescent probes can be applied to the detection of amino acids. Therefore, the study of small molecule fluorescent probe technique and its application in protein detection is very important. In this article we report two new coordination polymers based on N-[(3-Pyridine)-sulfonyl]amino acid: [Zn (L)•(4,4'-dipyridy)•H_2O]$_n$•n$H_2$0(1); [Zn(L)•(4,4'-azpy)•H_2O]n•2n$H_2$0(2).

2.Experimental

All solvents and chemicals were commercial reagents and used without further purification. N-[(3-Pyridine)-sulfonyl]amino acid(H_2L) was synthesized according to references.[18] Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin-Elmer 240 elemental analyzer. The emission spectra were recorded on Time-resolved fluorescence spectrometer FL3-TCSPC.The crystal structure was determined by a Bruker APEX-Ⅱ CCD diffractometer.

2.1 Synthesis of [Zn(L)•(4,4'-dipyridy)•H_2O]$_n$•n$H_2$0(1)

A mixture of Zn(NO_3)$_2$•6H_2O (0.0297 g, 1 mmol), H_2L(0.0219 g, 1 mmol), 4,4'-dipyridy (0.0156 g, 1 mmol) and 10 mL of 1:1 H_2O/ethanol was stirred at room temperature for 10 min under 40℃ temperature, 1 mol/L KOH solution was used to adjust pH to about 6, the

reaction continued for 3 h, and filtered. The filtrate was collected in a 25 mL beaker. One day later colorless massive crystals of 1 were obtained. Yield: 50% (based on Zn) . Anal. Calcd. (%) for $C_{17}H_{18}N_4O_6SZn$: C, 43.24; H, 3.82 N, 11.87. Found (%): C, 44.12; H,3.93; N, 11.71.IR(cm^{-1}): 3560w, 3279s, 1659w, 1586s, 1418s, 1396s, 1323m, 1196w,1163m, 1127 w, 1108m, 1067w, 960m, 855m, 817w, 753m, 694w, 661w, 573w, 533w.

2.2 Synthesis of [Zn(L)•(4,4'-azpy)•H_2O]$_n$•2n$H_2$0(2)

A mixture of $Zn(NO_3)_2$•$6H_2O$ (0.0297 g, 1 mmol), H_2L(0.0219 g, 1 mmol) and 10 mL of 1:1 H_2O/ethanol. The mixed solution was stirred for 10 min at room temperature, adjusted the pH about 6 with triethylamine solution, 5 mL 0.1 mol/L 4,4'-azpy was added to the mixed solution, then sealed in a 23ml Teflon-linged stainless steel container and heated at 120℃ for two days. The mixture cooled to room temperature at a rate of 10 ℃/h, colorless needle crystals of 2 were obtained, yield 70% (based on Zn).Anal. Calcd for $C_{17}H_20N_6O_7SZn$ (%): C, 39.39; H, 3.86; N, 16.22. Found: C, 40.08; H,3.91; N, 16.02.IR(cm^{-1}):3440s, 3225s, 3126w, 2379w, 1667s, 1604w, 1467m, 1432m, 1393m, 1338m,1300w, 1207m, 1170s, 1108s, 1048w, 965w, 905w, 872m, 812w, 773w, 751w, 694m, 607s.

2.3 Crystallographic Data Collection and Refinement.

Single-crystal X-ray diffraction data were collected on a Bruker SMART diffractometer equipped with a graphite-monochromatized MoKa radiation (λ=0.71073 Å) at 293(2) K. For **1** and **2**, the structures were solved by direct methods using the SHELXS-2013, and refined by full- matrix least-squares on F^2 using the Olex^2 program[19] and refined with Olex2 program[20]. All non-hydrogen atoms were refined anistropically. Hydrogen atoms were gene- rated geometrically and refined isotropically with the riding mode. Details of crystallographic data for these two coordination polymers are listed in Table 1, and their selected bond lengths and bond angles are given in Table 2. Hydrogen bonds for coordination polymers **1**-**2** are shown in Table 3. Crystallographic crystal data and structure

processing parameters for coordination polymer **1-2** are summarized in Table 1(SI). Selected bond lengths and bond angles for coordination polymer **1-2** are listed in table 2(SI), Hydrogen bonds for coordination polymer **1-2** are listed in table 3(SI). CCDC： 1474215, 1;1474216, 2.

3. Results and Discussion

3.1 Discussion crystal structure of coordination polymer 1

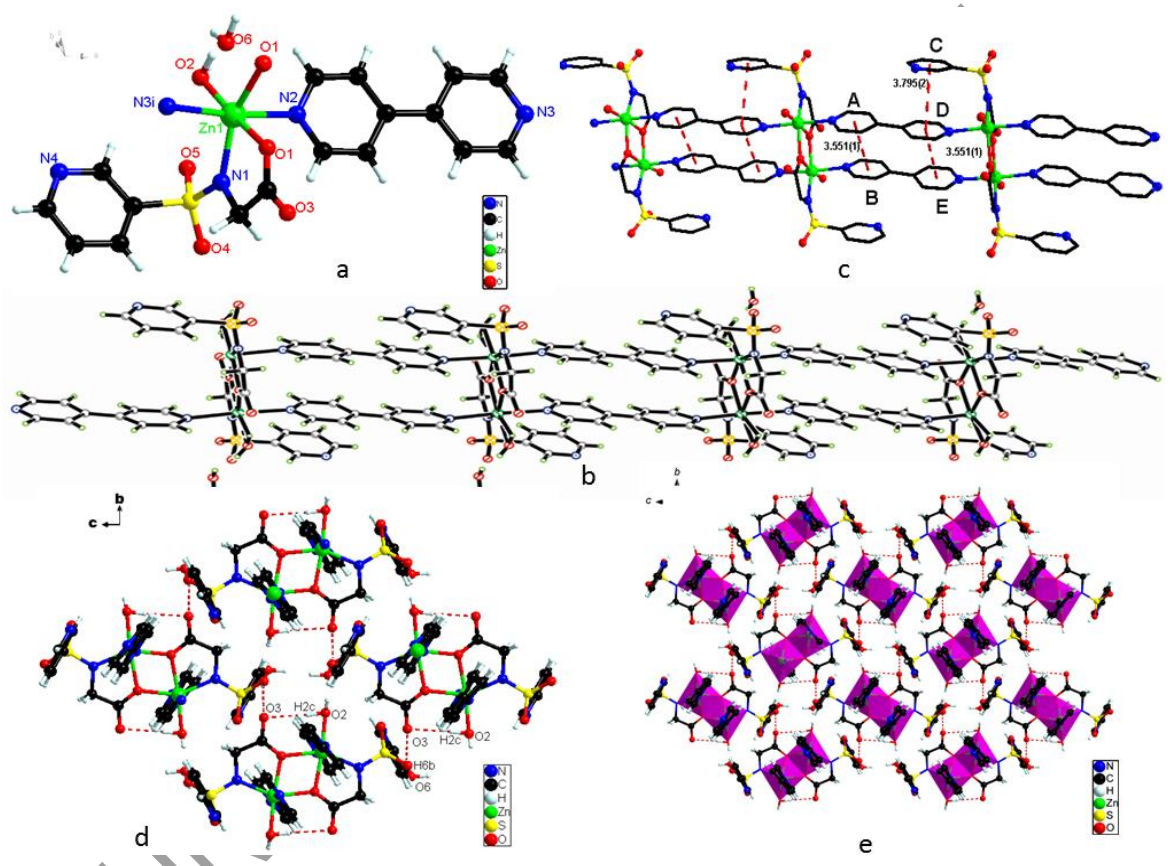

Fig.1 (a) The coordination environment of Zn(II) ions in **1** with thermal ellipsoids at 50% level.(b) one-dimensional chain was formed by 4,4-bipyridyl bridged Zn (II) of coordination polymer **1**. (c) π···π stacking interaction of polymer 1. (d) and (e) 2-D network structure of coordination polymer **1** was formed by hydrogen bonds viewed along the a-axis.

A single-crystal X-ray diffraction study reveals that **1** is a two-dimensional coordination polymer which crystallizes in the monoclinic, space group $P2_1/c$. The asymmetric unit contains one Zn(II) cation, one ligand anion, one 4,4'-dipyridy, one coordinated water molecule and one free water molecule. As illustrated in figure 1a, Zn(II) adopts a octahedral coordination environment, which is coordinated by three nitrogen atoms from 4,4'-dipyridy (N2,N3i) and sulfamine (N1) of ligand as well

as three oxygen atoms(O1, O1i) from two carboxylates of ligands, and one oxygen (O2) from coordinated water molecule. The center Zn (II) ion in 1 is six-coordinated. The Zn–O distances fall in the range of 2.076(4) ~ 2.150(3) Å(Zn1-O1=2.150(3)Å; Zn1-O1ii=2.124(3) Å; Zn1-O2=2.076(4) Å). The Zn–N distances fall in the range of 2.070(4) ~ 2.247(4) Å. (Zn1-N1=2.070(4) Å; Zn1i-N2=2.218(4) Å; Zn1-N3=2.247(4) Å). The bond angles of N2-Zn1-N3 and O2-Zn1-O1 are 172.53(14) and 174.20(18)°, respectively. These bond angles and bond distances all fall in the normal ranges. [21-22]

The bridging ligand of 4,4'-dipyridy was coordinated with two adjacent Zn(II) ions to form a two-dimensional network structure(Fig.1b). Notably, there are π•••π stacking interactions between 4,4'-dipyridy and pyridine ring of ligand (Fig.1c).The π•••π bond distance of 4,4'-dipyridy to 4,4'-dipyridy is 3.551(1) Å, but The π•••π bond distance of 4,4'-dipyridy to pyridine ring of ligand is 3.759(2) Å. Since the introduction of the water molecules, so that in 1 not only had the intramolecular hydrogen bonds, but also had intermolecular hydrogen bonds (Fig.1d). The coordinated water molecule(O2) and carboxyl oxygen atom(O3) forming O-H•••O hydrogen bonds. Meanwhile, the carboxyl oxygen atom(O3) and free water molecule(O6) forming O•••O-H hydrogen bonds. These hydrogen bonds and π•••π stacking interactions in 1 affect the stability of polymer structure. The Zn(II) ions in 1 can saw more clearly by the of distribution of metal ions polyhedron(Fig. 1e).

3.2 **Discussion crystal structure of polymer 2**

A single-crystal X-ray diffraction study reveals that **2** is a three-dimensional coordination polymer which crystallizes in the monoclinic, space group $P2_1/n$. The asymmetric unit conta ins one Zn(II) cation, one ligand anion, one 4,4'-azpy, one coordinated water molecule and two free water molecules.

As illustrated in figure 2a, Zn(II) adopts a octahedral coordination environment, which is coordinated by three nitrogen atoms from 4,4'-azpy (N2,N2i) and sulfamine (N1) of ligand as well as

three oxygen atoms(O1, O1i) from two carboxylates of ligands, and one oxygen (O2) from coordinated water molecule. The center Zn (II) ion in 2 is six-coordinated. The Zn–O distances fall in the range of 2.090(5)~2.151(6) Å(Zn1-O1=2.090(5)Å; Zn1-O2=2.091(6) Å; Zn1-O3=2.151(6) Å). The Zn–N distances fall in the range of 2.120(7)~2.208(6) Å. (Zn1-N1=2.120(7) Å; Zn1-N2=2.208(6) Å; Zn1-N3=2.147(7)Å). The bond angles of N3-Zn1-N2 and O2-Zn1-O1 are 172.2(3) and 177.8(2)°, respectively. These bond angles and bond distances all fall in the normal ranges.[21-22]

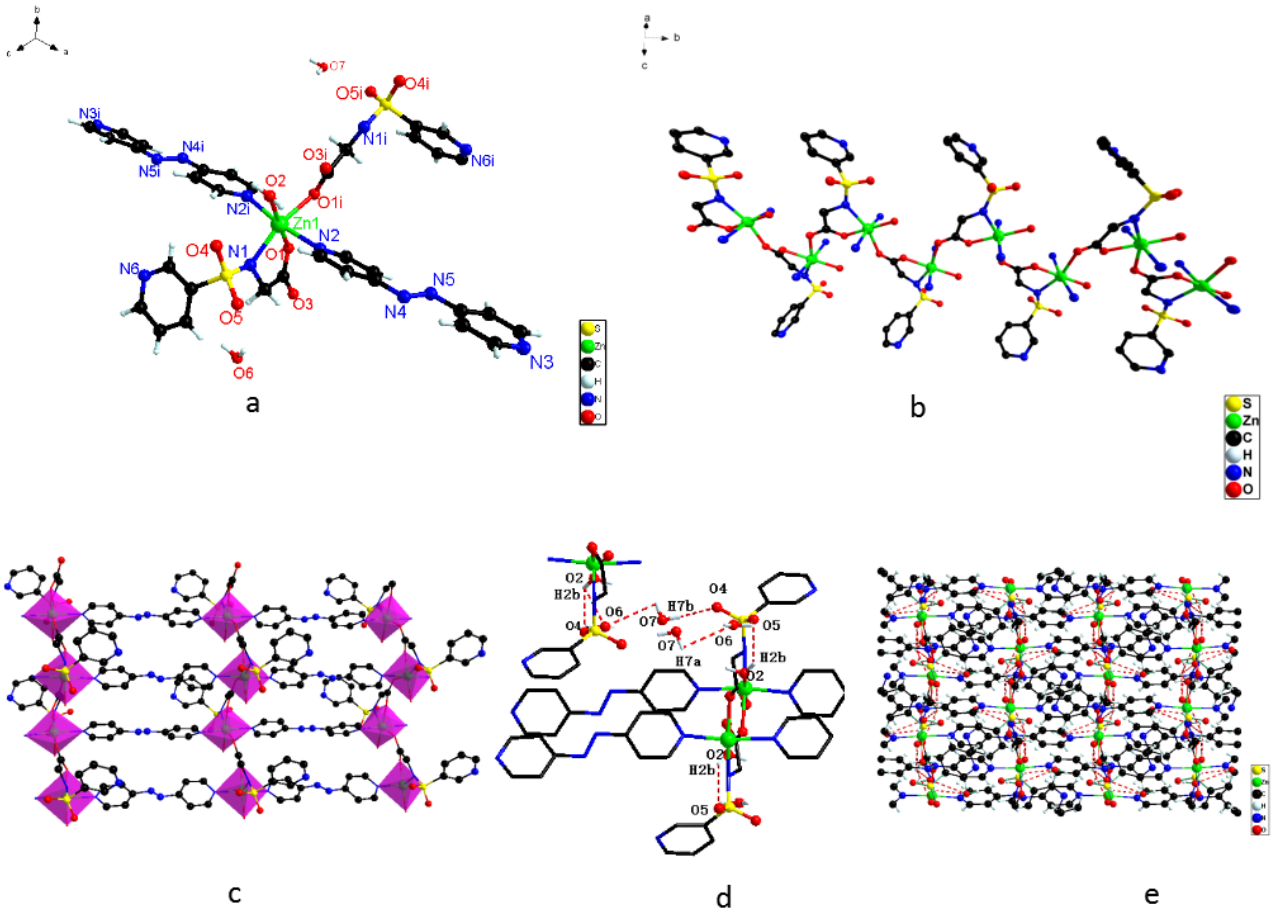

Fig.2 (a) The coordination environment of Zn(II) ions in **2** with thermal ellipsoids at 50% level.(b) One-dimensional chain was formed by carboxyl bridged Zn (II) in **2**. (c) Two-dimensional network structure was formed by 4,4'-azpy bridged Zn (II) in **2**. (d) Hydrogen bonds in **2**. (e) Three-dimensional structure of polymer **2** was formed by hydrogen bonds viewed along the c-axis.

The different between polymer **2** and polymer **1** is that carboxyl O atoms of ligand all are coordinated with Zn(II) ions. Two O atoms from carboxyl of ligand are coordinated with two Zn(II) ions, so carboxyl adopts μ_2-η^1:η^1 bridging style to form 1-D structure(Fig.2b). Bridging ligand of 4,4'-azpy was coordinated with two adjacent Zn(II) ions to form a two-dimensional network

structure(Fig.2c). Since the introduction of the water molecules, so that in **2** not only had the intramolecular hydrogen bonds, but also had intermolecular hydrogen bonds (Fig.1d). The coordinated water molecule(O2) and sulfonyloxy atom (O5) forming O-H•••O hydrogen bonds. Meanwhile, between the free water molecules(O6 and O7) and free water molecule(O7) and sulfonyloxy atom (O4) forming O-H•••O hydrogen bonds(Fig.2e). Three-dimensional structure was formed through hydrogen bonds (Fig. 2d).

3.2 XRD spectra

In order to check the purity of coordination polymers, powder X-ray diffraction of the a s-synthesized sample was measured at room temperature. The peak positions of experimental patterns are in good agreement with the simulated ones, which clearly indicates good purit y of the coordination polymers. The powder diffraction of polymer **1** is showed in (SI)-Fig. 1;The powder diffraction of polymer **2** is showed in (SI)-Fig.2.

3.3 Luminescence spectra

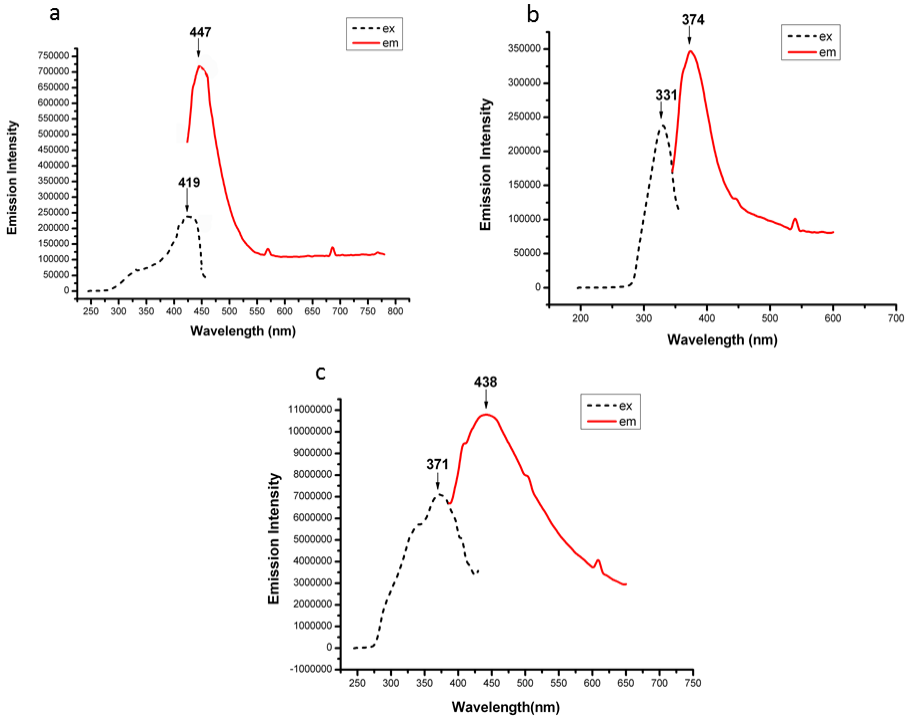

Fig.3 (a) The solid fluorescence spectra of ligand.(b)The solid fluorescence of ploymer **1**.(c)The solid fluorescence of ploymer **2**.

The ligand (H_2L) solid fluorescence spectrum was tested at room temperature under the conditions

of a slit width of 1nm (Fig.3a). As shown in figure can be seen that when the maximum excitation wavelength λex = 419nm, H2L in λem = 447nm has a maximum intensity fluorescent emission peak, which attributed to the transition of $\pi* \rightarrow \pi$ or $\pi* \rightarrow$ n of the ligand. After the ligand coordinated with Zn(II), blue-shifted emission peak has occurred and with a peak broadening, but not the same blue-degree shift. For example: polymer **1** in λem =374nm wavelength generated at a strong blue emission band (λex =331nm)(Fig.3b), the emission peak blue shifted 73nm.; polymer **2** in λem =438nm wavelength generated at a strong blue emission band (λex =371nm) (Fig.3c), emission peaks occurred a slight blue shift (the emission peak blue shifted 9nm.) These transmitters are come from the charge transfer between the ligand and metal (LMCT).These results may be assigned to coordination environments around the metal ion, since photoluminescence behavior is closely associated with the metal center and the ligands coordinated around it.[23-24]

4. Conclusion

In summary, in this paper the N-[(3-Pyridine)-sulfonyl]amino acid and $Zn(NO_3)_2 \cdot 6H_2O$ are as raw material, in the same ratio material and solvent, under different bridging ligand and reaction temperature, two-dimensional coordination polymer **1** was obtained at room temperature; three-dimensional coordination polymer **2** was obtained by hydrothermal synthesized. A structural comparison of these two coordination polymers suggests that different reaction temperatures play important role in the construction of resulting architectures for **1** and **2**. Fluorescence measurements show that **1** has medium fluorescent emission at 374 nm and **2** has medium fluorescent emission at 438 nm.

Acknowledgments. The authors acknowledge the financial support from the Scientific Research and Technological Development Project of Guilin (No. 20110330); Guangxi Natural Science Foundation (2014GXNSFAA118035); The project of education department of Guangxi province (No: YB2014331).

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